Sensor Needs and Requirements for Proton-Exchange Membrane Fuel Cell Systems and Direct-Injection Engines

Sponsored by
U. S. Department of Energy
Energy Efficiency and Renewable Energy
Office of Advanced Automotive Technologies

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May 2000

Cover Design by Frank Uhlig

Engine shown on the cover (top) is the Ford DIATA (Direct Injection, Aluminum, Through-Bolt Assembly) engine courtesy of Scott Low, Ford Motor Company

Fuel cell (bottom) is the International Fuel Cells, LLC PEM stack, gasoline reformer design, courtesy of Doug Wheeler, International Fuel Cells, LLC

Published by Lawrence Livermore National Laboratory Applied Energy Technologies Program P. O. Box 808 7000 East Avenue Livermore, California 94551

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Acknowledgements

This workshop would not have been possible without the commitment of the eighty engineers and scientists who participated. The participants are listed in Appendix A. We also appreciate the companies, universities, and government agencies who committed the resources, both time and money, which allowed their employees to attend the workshop.

Special appreciation is extended to the invited speakers: Tom Cackette (California Air Resources Board), Doug Wheeler (International Fuel Cells, LLC), Rich Belaire (Ford Motor Company), and Joe Stetter (Illinois Institute of Technology). We also thank the panel members for the breakout sessions. For fuel cells, the panel members were: Doug Wheeler, Joe Stetter, Fernando Garzon (Los Alamos National Laboratory), and Jacob Wong (Ion Optics, Inc.). For the CIDI/SIDI engines breakout the panel members were: Rich Belaire, Richard Cernosek (Sandia National Laboratories), Joe Giachino (Visteon), Brage Golding (Michigan State University), and Paul Raptis (Argonne National Laboratory). In particular, we would like to acknowledge the point contacts on the panels, Fernando Garzon and Rich Belaire, who collected input from the other panel members and provided draft summaries from the breakout sessions. Putting the draft summaries together was greatly facilitated by the excellent notes taken by Fernando and Jeff Griffin (Pacific Northwest National Laboratory). Outstanding facilitation of the breakout sessions was provided by Tom Coleman and Pat Chance from Lawrence Livermore National Laboratory. They kept us focused and on track.

Finally, the workshop would not have been possible without the administrative assistance provided by Jane Rubert and Lisa Henson from LLNL. They did the bulk of the behind-the-scenes work that made the workshop run smoothly and efficiently.

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Executive Summary

Workshop Objectives/Goals

On January 25 and 26, 2000, the Department of Energy (DOE) Office of Advanced Automotive Technologies (OAAT) sponsored a workshop on sensor needs for automotive fuel cell systems; compression-ignition, direct-injection (CIDI) engines; and spark-ignition, direct-injection (SIDI) engines. These technologies are being developed by OAAT under the Partnership for a New Generation of Vehicles (PNGV), a government-industry collaboration to develop vehicles having up to three times the fuel economy of today's mid-size automobiles.

The purpose of the workshop was to draw upon the expertise of the fuel cell development community, the DI engine community, and sensor researchers and manufacturers to define the needs and technical targets for sensors, and to aid DOE in identifying and prioritizing R&D activities in those areas. Sensors enhancing both proton-exchange membrane (PEM) fuel cell and CIDI/SIDI engine performance were of interest, as well as those for use in emission control, and for passenger safety. The objectives of the workshop were to:

- define the requirements for sensors
- establish R&D priorities
- identify the technical targets and technical barriers
- facilitate collaborations among participants

The recommendations from this workshop will be incorporated into the multi-year R&D plan of the DOE Office of Advanced Automotive Technologies.

Sensor Priorities and Requirements

Following the opening session, the workshop participants were divided into two working groups - one for fuel cells and one for CIDI/SIDI engines. Each group focused on the workshop goals identified above. For fuel cell systems, the high priorities are CO sensors which are needed to prevent fuel cell poisoning and hydrogen sensors for performance control and safety. For CIDI and SIDI engines, the highest priority is a NO_x sensor for emission control. For CIDI engines, sensors for control of particulate matter (PM) emissions are a high priority and wide-range oxygen sensors are a medium priority. A summary of sensor priorities and the technical requirements for each area are given below. Extended discussion for each sensor can be found later in this document.

SENSORS FOR AUTOMOTIVE PEM FUEL CELL SYSTEMS

Most commercially available sensor technologies have not been designed to operate in a fuel cell gas environment. The most common sensor design environment is ambient air, not fuel cell reformate gas streams. The major complaints are that the sensors that do work to varying degrees of success are too big and costly, and that sensors that are potentially low cost are not reliable or do not have the required lifetime. In some cases, neither performance nor cost targets can be met. Extensive research in redesign and

development is needed for operation in a fuel cell gas environment. Careful testing of prototype devices in fuel cell stack/fuel processor environments will be needed to validate the performance of any sensor. Research, development, and validation should be carried out through careful coordination among industry, national laboratory, and university sensor researchers, sensor manufacturers, fuel cell system developers, and the automobile industry. Prioritized sensor needs for proton-exchange membrane fuel cell systems operating on direct-hydrogen and on reformed fuels are listed in Table 1.

Table 1. Requirements for PEM Fuel Cell System Sensors^a

Sensor	Requirements		
Carbon Monoxide	a) <u>1-100 ppm reformate pre-stack sensor</u>		
	 Operational temperature: <150 °C 		
	Response time: 0.1 - 1 sec		
	 Gas environment: high humidity reformer/partial oxidation gas- H₂ 30-75%, CO₂, CO, N₂, H₂O at 1-3 atm total pressure 		
	Accuracy: 1-10 % full scale		
	b) <u>100-1000 ppm CO sensors</u>		
	 Operational temperature: 250 °C. 		
	Response time: 0.1 - 1 sec		
	 Gas environment: high humidity reformer/partial oxidation gas-H₂ 30-75%, CO₂, CO, N₂, H₂O at 1-3 atm total pressure 		
	Accuracy: 1-10 % full scale		
	c) <u>0.1-2% CO sensor 250 °C -800 °C</u>		
	 Operational temperature: 250 °C −800 °C. 		
	Response time: 0.1 - 1 sec		
	- Gas environment: high humidity reformer/partial oxidation gas- H ₂ 30-75%, CO ₂ , CO, N ₂ , H ₂ O at 1-3		
	atm total pressure		
	Accuracy: 1-10 % full scale		
Hydrogen in fuel processor	 Measurement range: 1-100% 		
product gas	 Operating temperature: 70- 150 °C 		
	Response time: 0.1 -1 sec for 90% response of step function		
	 Gas environment: 1-3 atm total pressure, 10-30 mol % water, total H₂ 30-75%, CO₂, N₂ 		
	Accuracy: 1-10 % full scale		
Hydrogen in ambient air	Measurement range: 0.1-10%		
(safety sensor)	— Temperature range: −30 to 80 °C		
	Response time: under 1 sec		
	- Accuracy: 5%		
	Gas environment: ambient air, 10 –98% RH range		
	- Lifetime: 5 years		
	Selectivity from interference gases such as hydrocarbons is needed		
Sulfur compounds	 Operating temperature: < 400 °C 		
(H ₂ S, SO ₂ , organic sulfur)	Measurement range: 0.05 ppm -0.5 ppm		
	Response time: < 1 min at 0.05 ppm		
	Gas environment: Hydrogen, carbon monoxide, carbon dioxide, hydrocarbons, water vapor		
Flow rate of product gas from	 Flow rates: 30 -300 standard liters per minute 		
fuel processor	 Temperature: 80 °C 		
	 Gas environment: high humidity reformer/partial oxidation gas: H₂ 30-75%, CO₂, N₂, H₂O, CO at 1-3 atm total pressure 		

Ammonia	Operating temperature: 70-150 °C
	Measurement range: 1-10 ppm
	Selectivity: <1 ppm from matrix gases
	Lifetime: 5-10 years
	 Response time: seconds
	- Gas environment: high humidity reformer/partial oxidation gas-H ₂ , 30-75%, CO ₂ , N ₂ , H ₂ O, CO at
	1-3 atm total pressure
Temperature	Operating range: -40- 150 °C
	Response time: in the −40-100 °C range < 0.5 sec with 1.5% accuracy; in the 100 − 150 °C range,
	a response time <1 sec with 2 % accuracy is sufficient
	 Gas environment: high humidity reformer/partial oxidation gas- H₂ 30-75%, CO₂, N₂, H₂O, CO at 1-
	3 atm total pressure
	Need to be insensitive to flow velocity
Relative humidity for cathode	 Operating temperature: 30-110 °C
and anode gas streams	- Relative humidity: 20-100 %
	– Accuracy: 1%
	- Gas environment: high humidity reformer/partial oxidation gas- H ₂ 30-75%, CO ₂ , N ₂ , H ₂ O, CO at 1-3
	atm total pressure
Oxygen concentration in fuel	(a) Oxygen sensors for fuel processor reactor control
processor and at cathode exit	− Operating temperature: 200-800 °C
	− Measurement range: 0-20% O₂
	- Response time: < 0.5 sec
	- Accuracy: 2% of full scale
	 Gas environment: high humidity reformer/partial oxidation gas- H₂ 30-75%, CO₂, N₂, H₂O, CO at 1-3 atm total pressure
	b) Oxygen sensors at the cathode exit
	Measurement range: 0-50% O ₂
	 Operating temperature: 30-110 °C
	Response time: < 0.5 sec
	 Accuracy: 1% of full scale
	 Gas environment: H₂, CO₂, N₂, H₂O at 1-3 atm total pressure
Differential pressure in fuel	 Measurement range: 0-1 psig or (0-10 or 1-3 psig - depends on design of fuel cell system)
cell stack	 Temperature range: 30-100 °C; -40 °C survivability
	Response time: <1 s
	– Accuracy: 1%
	Size: Needs to be small - 1 square inch and orientation cannot be a problem
	Other: has to be able to withstand and measure liquid and gas phases
a Concore must conform to size	weight lifetime and cost constraints required for automotive applications

^a Sensors must conform to size, weight, lifetime, and cost constraints required for automotive applications

SENSORS FOR CIDI/SIDI ENGINES

Sensors for CIDI/SIDI engines are at a more mature stage of development than fuel cell sensors. While the sensors identified below currently exist for defined applications, there are no sensors available that fall into the highest need category and meet all of specifications required by the automotive industry. These specifications include operation in very harsh environments, high sensitivity and selectivity, long lifetime, low/no maintenance, high stability, and low cost. In addition, sensors need to be developed for specific systems, not generic operation, because manufacturers sometimes have different measurement strategies. Requirements for the high priority NO_x and particulate matter (PM) sensors, and for the medium priority wide-range oxygen sensor are listed in Table 2 .

Table 2. Requirements for CIDI/SIDI Sensors^a

Sensor	Requirements
NOx	 20-300 ppm sensitivity for diesel (with potential for some applications up to 2000 ppm feed gas)
	 100-200 ppm sensitivity for gas engines
	 Measurement precision within ± 5 ppm for diesel and within ± 20 ppm for gas engines
	 Temperature: 600-1000°C
	 Lifetime: 10 years; 150,000 miles for automobiles and 500,000 miles for trucks
	 Response time: 1 sec or less (must be 5 ms for cylinder-to-cylinder monitoring and 50-100 ms for engine control)
	 Separate measurements of NO and NO₂
	 Immune to soot, sulfur and urea (NH₃)
	Cost < \$20.00
Particulate Sensor	Smoke number under 2 BSU (Bosch smoke units)
	 Minimum detection: 0.2 BSU
	 Temperature: 600-1000 °C
	 Lifetime: 10 years; 150,000 miles for automobiles and 500,000 miles for trucks
	 Response time: 1 sec or less (must be 5 ms for cylinder-to-cylinder monitoring and 50-100 ms for engine control
	— Cost < \$20.00
Wide Range O ₂ Sensor	 Range is λ from 0.7-15 (includes diesel)
	 Response better than 4 Hz for engine control
	 Temperature range: ambient - 1000°C
	 Startup time less than 15 seconds
	 Resistant to poisoning from phosphorous, sulfur, lead and particulates
	Cost ≤ \$20.00

^a Sensors must conform to size, weight and cost constraints required for automotive applications

May 2000

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Introduction

To reduce U.S. dependence on imported oil, improve urban air quality, and decrease greenhouse gas emissions, the Department of Energy (DOE) is developing advanced vehicle technologies and fuels. Enabling technologies for fuel cell power systems and direct-injection engines are being developed by DOE through the Partnership for a New Generation of Vehicles (PNGV), a government-industry collaboration to produce vehicles having up to three times the fuel economy of conventional mid-size automobiles.

Sensors have been identified as a research and development need for both fuel cell and direct-injection systems, because current sensor technologies do not adequately meet requirements. Sensors are needed for emission control, for passenger safety and comfort, to increase system lifetime, and for system performance enhancement through feedback and control. These proceedings document the results of a workshop to define sensor requirements for proton exchange membrane (PEM) fuel cell systems and direct-injection engines for automotive applications. The recommendations from this workshop will be incorporated into the multi-year R&D plan of the DOE Office of Advanced Automotive Technologies.

The workshop attracted more than eighty participants. They included representatives from DOE, the national laboratories, automakers, the California Air Resources Board, universities, PEM fuel cell developers, fuel processor developers, CIDI/SIDI engine developers and manufacturers, and sensor manufacturers. The success of the workshop can be attributed to the diversity and sound technical foundation contributed by the participants. A complete list of the attendees is given in Appendix A.

The workshop consisted of invited talks and breakout sessions. A complete agenda is given in Appendix B. The plenary session included presentations from DOE program managers, and invited overview presentations covering present and future emissions regulations (Tom Cackette, CARB); the state-of-development of PEM fuel cells (Doug Wheeler, IFC); the state-of-development of CIDI engines (Rich Belaire, Ford); and the sensor field (Joe Stetter, IIT). Following the plenary session, two concurrent facilitated breakout sessions were organized - one focused on sensor needs for fuel cells and the other on sensor needs for CIDI and SIDI engines. For each session, a panel was formed to help guide the discussions. At the beginning of each session, the panel members gave brief opening comments. Members of the general audience were also invited to make short presentations. Summaries of the presentations are included in the report; visuals from the presentations are provided in Appendix C.

During the breakout sessions sensor needs were identified and prioritized, and performance criteria were defined. A large number of chemical and physical sensors were considered. Technologies not traditionally classified as sensors (e.g., infrared spectrometers or ion mobility mass spectrometers) were also discussed. It was recognized that revolutions/evolutions in optical and electronic technology could make these types of technologies available in the not-too-distant future. However, at this point in time, the sensor field can be considered to be more evolutionary than revolutionary.

Decades of development have gone into the development of electrochemical, spectroscopic, acoustic, and thermal sensors for chemical detection, and physical sensors. In large part, the challenge lies in the further development of specific materials, packaging, integration, and particularly in developing systems that are cost effective. In the final analysis, the best sensor approach for automotive applications should be selected based upon consideration of the analyte, required operational specifications, cost, and probability of success.

I. Summaries of the Plenary Session Presentations

"Overview of the DOE Transportation Fuel Cell Program," JoAnn Milliken, DOE

To reduce U.S dependence on foreign oil, the Department of Energy (DOE) Office of Transportation Technologies (OTT), in partnership with industry, is developing advanced vehicle technologies and fuels. Fuel cells, with their high efficiency, lowto-zero emissions, and fuel flexible characteristics, have emerged as one of the most promising technologies to meet the challenge. Fuel cell vehicles operating on gasoline, methanol, ethanol, or natural gas offer a pragmatic near-term option that can use the existing fuel infrastructure and accelerate fuel cell technology commercialization in vehicle applications. They will provide a transitional pathway toward a more sustainable long-term future based on renewable hydrogen as the requisite infrastructure is put into place. While the OTT Fuel Cell Program has made tremendous progress during the past 5 years, significant technical challenges remain. Through both industry and national laboratory R&D, OTT is addressing those challenges which include reducing the size, weight, and cost of the fuel processor and fuel cell stack subsystems, and developing automotive balance-of-plant components including air compressors, sensors, and controls.

"Overview of the DOE SIDI Engine Program," Rogelio Sullivan, DOE

Spark-ignited, direct-injection (SIDI) engines have been the focus of intense research at various times in the past, and have been at the doorstep of full production in the U.S. more than once. The principal attraction of SIDI engines is their potential high efficiency that stems from their stratified charge, lean-burn operation. In principle, SIDI should be able to utilize higher compression ratio and require little if any throttling for load control.

One of the primary barriers preventing the introduction of SIDI engines to the U.S. market has been emissions. The emission problem is being addressed through an integrated approach that considers the fuel, combustion control, and emissions treatment. In addition to emissions, the excessive cost of the high-pressure injection hardware is another important hindrance to commercialization of the technology in the U.S.

The DOE SIDI R&D program was initiated in FY 1999. The objectives of the program are to conduct research to enable SIDI engine introduction in the U.S., support technology development for emission control, and to provide a fallback option for CIDI. Because the DOE engine portfolio is heavily weighted with CIDI research, and the CIDI engine faces enormous emission and other potential drawbacks, it seems prudent to

conduct enabling research on other high efficiency engine alternatives. The SIDI program is coordinated with the auto industry through the Low Emission Partnership (LEP) of USCAR. The program is reviewed and coordinated with the LEP on an ongoing basis.

The program's budget for FY 2000 is \$6.9 Million and there are three major program thrusts:

- Fundamental Combustion Research and Modeling (national labs and universities)
- Engine and Component Research (contractors and national laboratories)
- Sensor Development (national laboratories)

Most of the ongoing sensor development projects in the SIDI program are conducted through a Cooperative Research and Development Agreement (CRADA) with the Low Emission Partnership. This work is primarily focused on the development of HC and CO sensors for on-board diagnostics and potentially engine control. This sensor CRADA has been in place since 1994 and involves Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Argonne National Laboratory, and Sandia National Laboratories. The national laboratories have developed devices using a variety of novel sensing techniques, materials, and processing technologies. The automotive partners help to test and evaluate the sensors and provide guidance on technical targets and performance requirements. These CRADA projects will end in FY 2001.

This workshop will help to identify high priority sensor needs for SIDI engines. If a consensus can be reached on sensor needs during the breakout session and collaborative projects quickly formulated, then one or more new sensor projects may be added to the program this year. Potential projects will be screened for technology maturity, direct industry involvement, cost share, technical feasibility, and other program and policy factors.

"Overview of the DOE PNGV CIDI Combustion and Emission Control Program," Ken Howden, DOE

The Partnership for a New Generation of Vehicles, an industry-government consortium, has selected the compression-ignition, direct-injection (CIDI) engine as the basis for the development of hybrid electric mid-size passenger vehicles which will achieve up to 80 miles per gallon by 2004. The challenge in choosing this engine for the powertrain is to meet stringent Federal emissions standards while maintaining the high efficiency offered by the diesel cycle. The DOE contribution to this effort includes cooperative research with the automotive OEMs, suppliers, and the national laboratories in the areas of clean combustion and new emission control technologies. New R&D programs have also been established with U. S. diesel engine manufacturers to develop innovative emission control systems for CIDI passenger car engines. This technology will also be demonstrated on light trucks and sport utility vehicles for maximum impact across the light-duty fleet. Advanced petroleum-based fuels, a key element in optimized combustion and emission control system performance and durability, are also being

developed in a parallel program with major energy companies and the automotive industry.

"Driving Towards Clean Air: Countdown to Zero," Tom Cackette, California Air Resources Board

Although Los Angeles remains one of the smoggiest cities in the nation, progress in reducing ozone has been substantial. The annual peak ozone has been reduced by 50% over the past 10 years to 0.17 ppm (the clean air goal is 0.09 ppm). Progress in reducing fine particles has been less, with unhealthy levels present on about 250 days per year.

The key to improving air quality is reducing hydrocarbon (HC), oxides of nitrogen (NO_x) and fine particle emissions (PM). Emission reductions of HC and NO_x well over 50% are needed to meet the ozone air quality standard. Mobile sources contribute about two thirds of these smog-forming emissions. Diesel engines are also a major contributor of directly emitted fine particles, which have been identified as a cancer causing substance, as well as a contributor to ambient PM.

Cars and light trucks have been the largest single source of smog-forming emissions. As car and light truck emissions are reduced in compliance with low emission vehicle standards, diesel engines, including those used in trucks, farm and construction equipment, and non-road vehicles such as locomotive and ships, become the largest source of smog-forming emissions (mainly NO_x), and also contribute about 70% of the public exposure to ambient air toxic compounds.

To achieve clean air in California, we need a substantial portion of vehicles to have zero or near zero emissions. This is most viable in the car and light truck, and urban heavy truck, sectors. Everywhere else, the application of best available technology is needed.

Near zero emission passenger cars (Nissan Sentra CA, Honda Accord EX) are being sold in California now, as are battery-powered electric vehicles and hybrid electric vehicles with very low emissions. Nearly every major auto manufacturer has promised introduction of fuel cell vehicles by mid-decade, and a unique industry/government partnership has been formed to address introduction of this new technology, including fuel and fueling infrastructure implications. Natural gas engines already emit less than one half the emissions of a heavy-duty diesel. However, diesel engine exhaust gas treatment devices that reduce NO_x and PM are becoming commercially available which create the likelihood for both diesel and natural gas engines achieving near zero emissions. Fuel cell engines also appear viable for use in heavy vehicles, especially those urban vehicles such as transit buses that could be fueled with hydrogen at a central site. Cost reduction remains the biggest challenge. Finally, automobile technologies such as the 3-way catalyst are being applied to industrial engines and boats. All these technologies benefit from the availability of low sulfur gasoline and diesel fuel.

In summary, the clean-up of all types of mobile sources, ranging from big ships to weed whips, is progressing rapidly. Zero and near-zero emissions are achievable for the major sources, including cars and diesel trucks. Clean fuels have enabled the use of clean-up

technologies and pave the way for future innovations. Technology offers us a promising path to clean air.

"State of Development of PEM fuel cells," Doug Wheeler, International Fuel Cells, LLC

This presentation provided an overview of the three PEM fuel cell areas: Fuel Cells for Transportation Applications; Fuel Cells for Stationary Power Generation; and Fuel Cells for Portable Power Applications. PEM fuel cells for transportation offer the opportunity to replace the internal combustion engine (ICE) power source and to be used as auxiliary power units (APU). High efficiency and near zero emissions are two of the primary characteristics for both applications. The PEM-powered vehicle must also have a range comparable to the gasoline-fueled ICE and there is some indication that multiple fuel applications will become important.

Stationary power generation includes both residential applications and commercial applications. Power plants operating in the range 5 kW to 15 kW are suitable for the residential applications while the commercial applications will typically be in the range of 50 kW to 1 MW. High reliability, high efficiency, ultra-low emissions, and multi-fuel capability are primary characteristics for the PEM stationary applications.

PEM portable power plants are targeted for extended life with a rechargeable fuel and high power output. The power output would range from 5 watts to 1 kW while the fuel cells could be either mechanically or reversibly rechargeable.

Two major design concepts are being developed for PEM power plants: pressurized power plants operating at pressures as high as 4 bar and ambient pressure power plants operating near atmospheric pressure. The two concepts reflect two different methods for removing liquid water from the fuel cell. Pressurized fuel cells remove water through evaporation and entrainment of water droplets in the spent reactants. Pressurization is attained using a compressor/expander that requires a parasitic power of 10% to 20%. A high efficiency compressor/expander that can operate over the full range of power densities for the fuel cell has not been developed and is the subject of considerable research and development activities. On the other hand, ambient pressure power plants do not have this parasitic performance loss but require the development of bipolar plates that are porous and can wick the liquid water away from the fuel cell. The development of low cost porous bipolar plates is a focus of research for the ambient fuel cell power plants. Both the pressurized and ambient fuel cell power plants operate at 80 °C and the temperature limit appears to be a function of the membrane properties. The performance of the cells is very similar with the ambient fuel cell operating at 0.7 V @ 1000 mA/cm² on hydrogen and air with 90/60 utilization respectively. Full size automotive fuel cell stacks for both concepts, in the range of 40kW to 70kW, have been manufactured and tested in vehicles.

Fuel processing has been a major effort in the development of fuel cell power plants. Major components include the desulfurizer, fuel reformer, shift reactor, and preferential oxidizer. Desulfurization is a major technical hurdle with targeted sulfur levels of less

than 0.05 ppm. Two types of reformer technology are being pursued: (1) autothermal reforming (ATR) and/or partial oxidation (POX) and (2) catalytic steam reforming (CSR). The choice of reforming technology is dependent on the application with ATR/POX addressing transportation needs of low volume and because of the ability to reform high carbon content fuels such as gasoline and diesel. The CSR technology is used with stationary where methane and propane are the fuels of choice and high efficiency is critical.

The shift reactor reacts water (steam) and carbon monoxide exiting the reformer to form hydrogen and carbon dioxide. To date, over 3 million commercial hours have been demonstrated in stationary commercial fuel cell applications using Cu/Zn catalyst. Improvements are necessary to reduce the volume of the shift reactor and these improvements may include the use of precious metal catalysts such as those under development at Argonne National Laboratory.

Preferential oxidation, also called selective oxidation, reduces the remaining carbon monoxide in the fuel processor gas stream to levels compatible with the fuel cell, e.g., 10 ppm. Ammonia is formed in the ATR/POX and is not removed by preferential oxidation. An additional scrubbing system maybe needed to remove the ammonia.

PEM power plants approach the performance levels required for transportation, stationary, and portable applications. Key component issues for the PEM power plant to be resolved are cost, power density, and durability.

"Overview of the State-of-the-Art in CIDI Engine Technology," Rich Belaire, Ford Motor Company

A comparison was made between technologies of current CIDI engines in widespread use today and emerging designs. Primary distinguishing features are the move toward high-pressure, common rail fuel injection systems, variable geometry turbocharging, 4-valve per cylinder architecture and sophisticated exhaust aftertreatment devices concentrating on control of NO_x and particulate matter.

Analytical tools are being applied to guide the design of DI combustion systems with a view towards reducing engine-out emissions and improving NVH (noise, vibration, and harshness) while maintaining the fuel economy advantage of diesel engines. Examples of some of the latest European production engines were given.

"Sensors Overview," Joseph Stetter, Illinois Institute of Technology

The world of chemical sensors is highly diverse and spans disciplines from physics and materials science to analytical chemistry and biology. Modern sensors are built on many platforms producing optical, electrochemical, mechanical, and thermal signals that correlate with the chemical variable of interest. A complementary approach is the miniaturization of large instruments like mass spectrometers, IR spectrometers, and chromatographs. While these are not strictly chemical sensors, the end result can be the desired one, i.e. high performance, low cost, rugged, stable, and long life measurements

of the chemical variable needed for automotive process control, safety and environmental monitoring. The automotive requirements for gas measurement of CO, O₂, HCs, H₂S, NH₃, NO_x, PM, SO₂ and the like in a small, robust, and low cost package that can withstand the severe automotive environments is a tall order for existing sensors. However, chemical sensor technology is in all stages of development from laboratory curiosity to already performing some field applications. It is the latter that we need to develop and modify to meet the near-term needs of emerging automotive technologies making them more environmentally acceptable, with higher performance, and customer safe.

The proposed sensor program is extremely important to the success of the DOE mission and to the country. It is clear that more sensor activity occurs abroad in terms of conferences, programs, and in many fields sensors are imported. The DOE program strengthens the U. S. infrastructure in chemical sensor development and will result in new developments that are enabling to the new advanced automotive technologies. Guidelines for preparation of proposals as well as the evaluation of the work need to be developed based around sound chemical sensor science and the principles of analytical chemistry. The current workshop will go a long way toward defining the appropriate goals for our sensors. Future workshops can focus on initial results and on equitable formulas for evaluation and benchmarking our progress on the important technology developments in chemical sensors for advanced automotive applications.

II. Fuel Cell Sensors

A. Breakout Session – Presentation Summaries

Doug Wheeler (International Fuel Cells, LLC):

Diagnostic sensors are at an early stage of development for PEM fuel cells; a large number of sensors are needed.

Sensors currently used:

- thermocouples for the stack- 70-90 °C; reformer; low temperature shift reactor; POX reactor; heat exchangers. Thermocouples are probably adequate
- pressure
- differential pressure
- mass flow
- liquid level
- temperature switches
- level switches
- flow switches
- O₂/air utilization (0-20%)-now using a high temperature oxygen sensor
- water conductivity, fluoride ion also used for diagnostics

Sensors that need development:

- hydrogen sensors
- CO sensors (0-500 ppm)

Fernando Garzon (Los Alamos National Laboratory):

- reconfigured electrode structures are more CO tolerant by an order of magnitude with respect to previous designs
- sensor for measurement of CO in H₂ still needed
- reliable H₂ sensor needed
- reliable mass flow sensors are also needed

Shuh-Haw Sheen (Argonne National Laboratory):

 For a hydrogen sensor, acoustic sensor using sound velocity and attenuation is potential method-hydrogen has a very high sound velocity in comparison to other gases. However, cost needs to be lowered for market acceptability.

Jacob Wong (Ion Optics, Inc.):

- Non-Dispersive Infrared (NDIR) gas sensor technology should not be misconstrued to be the same technology as IR spectrometers used in a laboratory setting. The latter are expensive, fragile, and bulky instruments that make very precise gas concentration measurements. NDIR gas sensors are an evolutionary product of IR gas sensors that have emerged over the last decade. NDIR sensors are small, rugged, sensitive, and inexpensive and have performance which in some cases is better than their "IR spectroscopic" counterparts
- NDIR is a viable technology that should not be overlooked. Detection limits for CO are good; and it may also be possible to simultaneously measure other gases present such as CO₂, H₂O, HCs, NH₃, etc.

B. Sensor needs, priorities, and technical requirements

Following the introductory comments by the panel and audience, the breakout session endeavored to answer the following questions:

- What do we want the sensors to measure/detect?
- What are the technical and performance targets?
- Are currently available sensors adequate/appropriate?
 - (a) If they are not, how can they be modified or improved?
 - (b) If none are available, how do we develop new sensors?
- What are the barriers to development of new sensors?
- What organizations are best suited to develop new sensors?

In general, it was the consensus that most commercially available sensor technologies have not been designed to operate in a fuel cell gas environment. The major complaints are that the sensors/instruments that do work, to varying degrees of success, are too big and costly and the sensors that are potentially low cost are not reliable or do not have the required lifetime. In some cases, neither combination of specifications can be met. The most common sensor design environment is ambient air, not fuel cell reformate gas streams. Extensive research in redesign and development are needed for operation in a fuel cell anode gas environment. Careful testing of prototype devices in fuel cell /fuel processor environments will be needed to validate the performance of any sensor. The research, development, and validation should be carried out by careful coordination between industry, national laboratory, and university sensor researchers, the device manufacturers, fuel cell component manufacturers, and the automotive industry.

Sensor needs were determined by polling the audience. The sensor needs were then prioritized by voting on the initial list of 26, some of which were combined. After the top priorities were identified, the breakout session participants divided into smaller groups to discuss the specific sensor requirements. These were then presented to the entire group for further discussion/clarification. The results are listed according to the number of votes received in descending priority, along with the identified requirements.

Priority 1: CO sensors for various concentration ranges and environments

CO sensors were considered the most vital sensor need for PEM fuel cell operation because of anode poisoning that occurs when concentrations of 5-100 ppm of CO are present in the fuel gas stream. Based upon input from fuel cell developers, CO sensors for three different operational regimes were identified. The sensors and their requirements are:

a) 1-100 ppm reformate pre-stack sensor

- Operational temperature: <150 °C

- Response time: 0.1 - 1 sec

Gas environment: high humidity reformer/partial oxidation gas- H₂ 30-75%,
 CO₂, CO, N₂, H₂O at 1-3 atm total pressure

For reformed gasoline the composition is:

Component	Before SOX (PROX)	After SOX (PROX)
H_2	34.8	32.1
H_2O	28.6	29.1
CH ₄	0.4	0.4
CO	0.7	<10 ppm
CO_2	14.8	14.9
N_2	20.4	23.2
Ag	0.3	0.3

- Accuracy: 1-10 % full scale

b) <u>100-1000 ppm CO sensors</u>

Operational temperature: 250 °C.

- Response time: 0.1 - 1 sec

Gas environment: high humidity reformer/partial oxidation gas-H₂ 30-75%,
 CO₂, CO, N₂, H₂O at 1-3 atm total pressure

- Accuracy: 1-10 % full scale

c) 0.1-2% CO sensor 250 °C -800 °C

- Operational temperature: 250 °C −800 °C.

- Response time: 0.1 - 1 sec

Gas environment: high humidity reformer/partial oxidation gas- H₂ 30-75%,
 CO₂, CO, N₂, H₂O at 1-3 atm total pressure

- Accuracy: 1-10 % full scale

The following technologies were identified as being commercially available: metal oxide semiconductor resistive sensors, IR spectroscopic devices, low temperature electrochemical sensors (not based upon the ion-conducting ceramic oxides used for current automotive applications), and colorimetric – dye based devices. All of these devices have limitations as identified in Table 3 below. Potential solutions that could be employed to make the current sensors useful for the CO sensing applications are provided.

Table 3. Available Sensors and Their Limitations for PEM Fuel Cell Applications

	MOS sensors	IR spectroscopic	Electrochemical	Colorimetric
Problems	Do not work in	First generation technology	Designed for air	Poor accuracy;
	reducing	was expensive, had limited	monitoring;	temperature and
	environments;	lifetime, and window	operating	lifetime
	humidity	fouling.	temperature and	limitations
	interference, cross	_	lifetime	
	sensitivity		limitations	
Solutions	Need new	Claims that new NDIR	Redesign for	Need new CO-
	semiconductor	technology is now available	fuel gas	sensitive dyes
	materials	and should be tested. Down	environment;	
		the road, third generation	need high	
		technology - lower cost	temperature	
		"spectrometers on a chip"	electrolytes	
		may become available		

This table does not imply that simple solutions for current technologies are available to make them useful for CO sensors. The entire list of specifications must be met and we have only highlighted important but partial solutions. There are a number of technical barriers that prevent current sensors or instruments from meeting the needs, and citing all of these and the potential solutions is beyond the scope of this document. Indeed, there is

not universal agreement on all the required specifications among the engineers from different companies who design fuel cell systems. Collaborative R&D programs including sensor designers (industry, national laboratories, universities) and end users were identified as ways to develop new CO sensors; currently available technologies probably cannot be simply modified to meet performance and cost needs. The major non-technical barriers to development are research costs and market size, which translates into risk for business.

Priority 2: Hydrogen sensors for product gas

A hydrogen sensor for fuel gas quality measurement was also identified as a very high priority. The operating conditions are as follows:

- Measurement range: 1-100 % hydrogen concentration

- Operating temperature: 70- 150 °C

- Response time: 0.1 -1 sec for 90% response

Gas environment: 1-3 atm total pressure, 10-30 mol % water, total H₂ 30-75%, CO₂, N₂ (see table above for CO sensors)

- Accuracy: 1-10 % full scale

Numerous hydrogen-sensing technologies are available including thermal conductance, MOS semiconductor sensors, electrochemical sensors, palladium thin film resistance sensors, and acoustic sensors. Operating temperature, cross sensitivity, and cost are the major barriers to implementation. Validation in fuel cell environments is expensive and strongly needed. Sensor manufacturers, national labs, universities, and fuel cell manufacturers may conduct research.

Priority 3: 1% hydrogen in ambient air, safety sensor

A hydrogen sensor that operates in the 0.1 to 10 % hydrogen concentration range was also identified as a major need because of the potentially explosive nature of hydrogen/air mixtures. This sensor would operate in the ambient environment, i.e., inside the passenger compartment of the fuel cell-powered vehicle.

− Temperature range: −30 to 80 °C

- Response time: under 1 sec

- Accuracy: 5%

- Gas environment: ambient air, 10 –98% RH range

- Lifetime: 5 years

- Selectivity from interference gases such as hydrocarbons is needed

Many sensor technologies were identified. The two most common commercially available technologies are MOS sensors and electrochemical sensors. These sensors need to be validated for cross sensitivity, lifetime and accuracy. Existing suppliers working closely with the fuel cell manufacturers and the transportation industry might develop the ambient air hydrogen gas safety sensor.

Priority 4: Sensors for sulfur-containing molecules

Very low levels of sulfur (from H₂S, SO₂ and organic sulfur) can adversely affect the performance of PEM fuel cells. Sensor requirements are:

- Operating temperature: < 400 °C

- Measurement range: 0.05 ppm -0.5 ppm

- Response time: < 1 min at 0.05 ppm

- Gas environment: see table above for CO sensors

It was the consensus from the fuel cell manufacturers that this sensor is needed upstream from the ATR/POX and fuel cell. Therefore, the sensor would be used as a sulfur detector in the fuel line. Alternatively, the detector could be at the exit of the desulfurizer or entrance to the ATR/POX where it would be a gas phase detection unit.

Existing technologies consists of electrochemical hydrogen sulfide sensors and spectrometric methods. Current technology is not designed to operate in the fuel cell environment.

Elimination of sulfur in the liquid fuel supplied would reduce the need for this sensor. Sensor manufacturers, national labs, universities, and fuel cell manufacturers might conduct research.

Priority 5: Flow rate sensors - product gas

Knowledge of the flow rate of the product gas from the fuel processor is needed for system feedback control. Operational requirements are as follows:

- Flow rates: 30 -300 standard liters per minute
- Temperature: 80 °C. (This is valid at exit of fuel processor; a flow sensor in the fuel processor is not recommended)
- Gas environment: high humidity reformer/partial oxidation gas: H₂ 30-75%,
 CO₂, N₂, H₂O, CO at 1-3 atm total pressure

The following existing technologies were identified: differential pressure sensors; thermal mass hot wire; magnetic sensing; and acoustic methods. All methods face

problems with variable gas composition, two-phase gas/liquid flow, and condensation at high humidity. Without initiating new sensor development efforts, current sensor manufacturers working together with the fuel cell manufacturers may be able to adapt existing technology. One barrier to development is market demand.

Priority 6: Ammonia gas sensor

Ammonia is an unwanted chemical byproduct originating from reaction of nitrogen in injected air streams with hydrogen gas. It inhibits fuel cell performance and measurement is desirable from a fuel cell performance standpoint. Sensing requirements are as follows:

Operating temperature: 70-150 °C

- Measurement range: 1-10 ppm

- Selectivity: < 1 ppm from matrix gases (see table for CO sensors)

- Lifetime: 5-10 years

- Response time: seconds

Gas environment: high humidity reformer/partial oxidation gas- H₂ 30-75%,
 CO₂, N₂, H₂O, CO at 1-3 atm total pressure

Available sensor technologies include MOS sensors, electrochemical sensors, IR spectroscopic, chemiresistive devices, and surface acoustic wave devices. The currently available technology is either not designed to operate in a fuel gas environment or is prohibitively expensive. Partnerships with fuel processor developers and sensor developers (industry, national labs, and universities) are necessary to develop sensors meeting necessary requirements.

Priority 7: Temperature sensors

Fast responding temperature sensors are needed throughout the fuel processor and the fuel cell stack.

- Operating range: -40-150 °C
- Response time: in the -40-100 $^{\circ}$ C range < 0.5 sec with 1.5% accuracy; in the 100-150 $^{\circ}$ C range, a response time <1 sec with 2% accuracy is sufficient
- Gas environment: high humidity reformer/partial oxidation gas- H₂ 30-75%,
 CO₂, N₂, H₂O, CO at 1-3 atm total pressure
- Must be insensitive to flow velocity

Existing technology includes thermocouples, RTD's, thermistors and IR sensors. The major problem with these current technologies is response time and cost. Temperature

sensor manufacturers can collaborate with fuel cell manufacturers to customize their products for the specific needs.

Priority 8: Relative humidity sensors

- Fuel cell membranes need constant humidification for proper operation. A
 humidity sensor may be needed for both cathode and anode gas streams.
- Operating temperature: 30-110 °C
- Relative humidity: 20-100 %
- Accuracy: 1%
- Gas environment: high humidity reformer/partial oxidation gas- H₂ 30-75%,
 CO₂, N₂, H₂O, CO at 1-3 atm total pressure

Current technology includes thin film capacitance sensors, resistive sensors, and dew point systems. Problems with existing technology include operating temperature (limits at 60-65 °C) and response time, and high relative humidity measurements are problematic. Partnerships with fuel processor developers and sensor manufacturers may help to develop these devices.

Priority 9: Oxygen concentration sensors

- (1) Oxygen sensors are needed for fuel processor reactor control purposes.
- Operating temperature: 200-800 °C
- Measurement range: 0-20% O₂
- Response time: < 0.5 sec
- Accuracy: 2% of full scale
- Gas environment: high humidity reformer/partial oxidation gas- H₂ 30-75%,
 CO₂, N₂, H₂O, CO at 1-3 atm total pressure

(2) Oxygen sensors are also needed at the cathode exit

- Measurement range: 0-50% O₂
- Operating temperature: 30-110 °C
- Response time: < 0.5 sec
- Accuracy: 1% of full scale
- Gas environment: H₂, CO₂, N₂, H₂O at 1-3 atm total pressure

High temperature electrochemical oxygen sensors are available from automotive suppliers. However, these types of sensors need to be validated in fuel cell gas operating environments. Low temperature electrochemical oxygen sensors are also available. These also need to be validated in cathode-exit gas environments. Oxygen sensor manufacturers can collaborate with fuel cell manufacturers to customize their products for specific needs.

Priority 10: Differential pressure sensors

Accurate, sensitive differential pressure sensors are desirable for use in the fuel cell stack for aiding in water management. These sensors need to have accuracy in inches of water.

- Measurement range: 0-1 psig and 0-10 psig (low range for atmospheric fuel cells and high range for pressurized fuel cells)
- Temperature range: 30-100 °C; -40 °C survivability
- Response time: <1 s
- Accuracy: 1%
- Size: Needs to be small 1 square inch and orientation cannot be a problem
- Other: has to be able to withstand and measure liquid and gas phases

Current technology is strain gage differential pressure technology. However, these sensors are expensive, large, and fragile. Need suppliers to be engaged in product development. Motorola and EG&G might have sensors to test.

III. CIDI and SIDI Engine Sensors

A. Breakout Session - Presentation Summaries

Joseph Giachino (Visteon):

- It's possible to consider over twenty potential powertrain sensor applications including air flow, pressure (air, fuel, oil), position (valves, cams, throttle, pedals, transmission gear), speed (transmission, vehicle), torque, and oil quality
- Sensors need to be combined
- Make direct measurements of property, not an indirect measurement (e.g., measure air/fuel ratio directly)

Sensor components:

- Sensing element
- Signal conditioning electronic

- Interface electronics
- Housing (includes connector)
- Get manufacturing people involved before starting sensor development process

Important sensor properties:

- Survivability (10 years and 150,000 miles, no cleaning or maintenance required)
- Selectivity
- Sensitivity

Sensor trade-offs:

- Accuracy
- Speed of response
- Robustness
- Span
- Cost

Richard Cernosek (Sandia National Laboratories)- "Overview of Sensor Projects at the National Laboratories"

Richard Cernosek gave an overview of the sensor activities occurring in the DOE national laboratories. There are a number of sensor development efforts underway, including:

- Vehicle exhaust gas constituent sensors
- Other gas sensors: NO_X, CO, HCs, O₂, H₂
- Particulate counters
- Pressure monitors
- Fluid monitors
- Rotation/position sensors

SNL Sensor Development

- Participant in Exhaust gas sensor CRADA: CRADA involves SNL, LLNL, and LANL. ANL is a team member under a separate CRADA. Engine testing with USCAR for use as OBD II sensors. Sandia emphasis has been on HC sensors. Acoustic wave technology for hydrocarbon monitoring using AT-cut, thickness shear mode crystals with sol-gel coatings to obtain high surface area
- Silicon MEMs pressure devices (not yet applied to automotive)
- Oil viscosity monitor using quartz resonator technique has been tested on automobiles.
- Micromachined catalytic gas sensor: polysilicon filaments 2 microns thick by 10 microns wide ... detects combustible gases

LANL Sensor Development

 Exhaust gas sensor CRADA. LANL emphasis has been on HC sensors and secondarily on CO sensors. Technology is based upon ceramic oxide sensors

- using zirconia and operating at 400-900 $^{\circ}$ C. "Spark plug" type design. Fast light-off. Detect H₂, CO, hydrocarbons, NO_X. 3000 hours of laboratory testing
- Lean burn oxygen sensors...linear amperometric O₂ sensors with porous metal oxide...linear response up to 25% O₂

LLNL Sensor Development

- Exhaust gas sensor CRADA. LLNL emphasis has been on HC sensors. New ceramic oxide electrochemical sensors for hydrocarbons using proton conducting electrolytes and differential catalysis are being developed. Oneto-one response between sensor response and FID detection for hydrocarbons obtained in engine dynamometer testing. Response times on the order of 1 second and sensitivity below 25 ppm demonstrated
- Also developing a new electrochemical NO_x sensor based upon differential catalysis and ceramic oxide materials
- In past work, also investigated linear oxygen sensors and fiber optic Fabry-Perot pressure sensor

ANL Sensor Development

- Participant in interlab exhaust gas sensor CRADA. Use miniature ion mobility technology for hydrocarbons and NO_x. Also developing millimeter wave technology for NO_x measurement (rotational absorption of dipolar gases, compact cavity or microstrip resonators, immune to particulates or sulfur contamination)
- Has concept for ultrasonic particle monitoring system using acoustic attenuation.
- In-cylinder piezoelectric sensor for pressure monitoring

ORNL Sensor Development

– Developing a solid state electrochemical sensor for NO_x for lean burn gasoline engines and another for diesel

PNNL Sensor Development

- Aqueous tape casting system, electrochemical, novel materials design and synthesis, sensor testing and evaluation

LBNL Sensor Development

Developing diesel particle scatterometer based on polarized light scattering

Miscellaneous

- Hydrogen gas sensor development is being conducted at SNL, LLNL, ORNL, and NREL
- Sensor arrays for vapor detection are being pursued at SNL, ANL, PNNL, and ORNL. These systems have potential use as fuel composition monitors. These monitors use pattern recognition and/or neural networks

 Numerous labs are working on non-contact rotation and position sensors such as planar Hall effect (SNL), giant magnetoresistance effect (ORNL), and rotary differential capacitance transducers (ORNL).

Paul Raptis (Argonne National Laboratory):

"Advanced Sensors for Automotive Engine Control." Areas under investigation:

- Focus on tailpipe exhaust emission sensors...ion mobility, millimeter-wave spectroscopy, acoustic and SAW/FPW chemical sensors are being pursued in the exhaust sensor CRADA
- Leak detection and location of pressurized components...micro-mass spectrometer, millimeter wave imaging, SAW
- In-cylinder sensors
- Air/fuel control system...intelligent valves
- Microwave cavity pressure sensor...deflection of diaphragm is proportional to pressure
- SAW flow sensor based on measurement of thermal conductivity change in a gas mixture
- Microwave dielectric sensor for engine oil quality monitoring
- Argonne ultrasonic viscometer...impedance and sound velocity measurements
 Ultrasonic particulate monitor...changes in sound velocity and acoustic
 attenuation
- Acoustic temperature sensor for catalytic converter which uses thin sensor materials with minimal impact on flow
- Millimeter wave proximity sensor...uses FM-CW radar technique for proximity sensing

Brage Golding, Michigan State University, NSF Center for Sensor Materials-"University Research in Automotive Sensors"

- Interdisciplinary sensor development does not fit well in an academic setting, hence the advantages of NSF multidisciplinary centers
- Air flow: wall-mounted sensor for flow rates and cumulative flow in unsteady ducts...MEMs-type device
- Hydrocarbon sensors being investigated:
 - Semiconductor MIS-Catalytic gate hydrocarbon sensor...use SiC...wide bandgap semiconductor with Pt catalytic gate-oxide barrier-SiC substrate-Pt backing layer
 - Molecular imprinting-thin, rigid polymer films via templating...expose polymer to analyte, polymerize and remove template, expose polymer template to analyte...use on SAW device to provide selective adsorption
- Oxygen sensor-inorganic chromophores for oxygen sensing in extreme environments...uses high temperature chromophores
- Fuel distribution

Spatial and time dependent injection of fuel...can look at phase of injected species...laser induced exciplex fluorescence visualization. Tag the spray with a tracer that reports independent information about liquid and vapor phases. Optical emission is different for vapor and liquid phases. Nice visuals showing detection of fuel spray concentration 550 microseconds after injection

Frank Zhao (Daimler-Chrysler):

"Diesel Closed-Loop Control via Smoke Sensor"

- Objective : Avoid hesitation during acceleration while controlling emissions.
 - Well-known trade-off between NO_X and particulate generation.
 - NO_X always decreases with increasing EGR rate
 - NO_X and oxygen are correlated with PM, but still require some assumptions
 - Enough EGR to reach PM limit will always produce the lowest NO_X
 - PM is highly non-linear near the PM limit
 - Can provide compensation for both fuel and engine component tolerances
- Choice between in-cylinder and tail pipe sensors. Daimler-Chrysler prefers a
 tail-pipe sensor because it allows monitoring the behavior of all cylinders.
 Daimler-Chrysler also thinks a smoke/PM sensor to be more useful than NO_X
 sensor.
- Required PM sensor performance:
 - A highly non-linear signal change near the PM-limited A/F giving a neardigital characteristic
 - Output signal proportional to the smoke level continuous from 0 to 5 BSU (Bosch smoke units)
 - Output signal to be independent of sensor temperature or other exhaust gas components
 - Could be used as an OBD device...
 - Maximize EGR rate under all speed/load conditions subject to a PM-level constraint
 - Full load fuel control...control full load fuel via PM level feedback rather than a preset fuel quantity based on worse case conditions. Compensate for injector wear-drift over time. Altitude compensation. Minimization of effect of part-to-part variations
 - A sufficiently fast response sensor could identify cylinder-to cylinder smoke variations and compensate
 - Pilot injection function diagnostic
 - Transient sensor response could be used for tuning manifold filling models
 - Optical sensors are not acceptable...Daimler/Chrysler did some work a
 while back on an electrical sensor for smoke detection...apparently the
 sensor wasn't very reliable

Prabir Dutta (Ohio State University):

Center for Industrial Sensors and Measurements (CISM) is investigating:

- Micro-polymeric device manufacture (for life sciences application)
- Micro-ceramic device manufacture (for hostile environments)
- System integration into arrays
- Education...this is an NSF Center
- CO sensor is based on TiO₂ ... anatase and rutile
- Second generation of CO sensors...selectivity through percolation
- NO sensor...planar design...electrochemical...insensitive to oxygen...use zeolite catalyst on one end of the sensor. Possible spark plug application
- Hydrocarbon sensor...electrochemical, uses a protonic conductor (sulfates and phosphates) and catalyst

Rick Soltis (Ford Research Laboratory):

Concentrating on zirconia-based NO_X Sensors

- NO_X sensors are needed for feedback control and monitoring
- Diesel engine applications
- HC injection NO_X diesel treatment
- Urea-based NO_X diesel treatment
- Feedback control
- Diagnostics (OBD for diesels)
- Operating principle: decomposing NO_X into N_2 and O_2 in low O_2 partial pressure and measuring the produced O_2 (which is proportional to NO_X) Device can also function as an oxygen sensor. Operates 750-800 $^{\rm o}$ C. Gets similar response for NO and NO_2 with this sensor
- Issues are durability, sensitivity, selectivity (sensor responds to ammonia), poisoning by soot and sulfur, response time, cost

Dave Gardner (Nexum Research Corporation):

"Combustion monitoring through Exhaust Temperature Waveform Analysis (ETW)." Vapor temperature sensors for exhaust gases and in-cylinder usage under development. Correlated cylinder pressure waveform with exhaust temperature waveform

<u>Harold Schock,(Michigan State University):</u>

"Mass Airflow Sensor Studies"

- Visualization of intake system dynamics
- LDV flow measurements using a controllable oscillating flow rig
- Every unsteady flow is different...one calibration can't fit all situations
- Developing a smart sensor to make time accurate measurements of mass

- flow rates in unsteady duct flows...uses silicon micro-machining
- Develop solutions to the unsteady Navier-Stokes equations

B. Sensor needs, priorities, and technical requirements

During the CIDI/SIDI breakout session sensor needs were identified through open discussion. The group then characterized the need for sensors as high, medium, or low priority. The group discussed in greater detail the requirements for the sensors that ranked highest.

Questions to answer for each proposed sensor:

- What are the technical and performance targets?
- Identify appropriateness/adequacy of current sensors.
- If a current sensor is suitable, identify improvements needed. If no current sensor is useful, how should a new sensor be developed?
- What are the barriers?
- What organizations are best suited for development, and how should organizations collaborate?
- What resources are required?
- What is the cost target?

The high priority sensor needs for CIDI/SIDI engines are NO_x and PM sensors. Widerange oxygen sensors are medium priority. Requirements, recommendations, and issues for NO_x , PM, and wide-range oxygen sensors are described below. A summary of all CIDI/SIDI sensors discussed at the workshop is provided in Table 4.

NO_x Sensors

Requirements:

- Sensitivity requirement (diesel): 20-300 ppm (potential for some applications up to 2000 ppm feed gas)
- Measurement precision: 5 ppm
- For gas engines, sensitivity shifts to 100-200 ppm and accuracy needs to be +/- 20 ppm
- Temperature: 600-1000 °C
- Lifetime: 10 years, 150K miles (for trucks, lifetime requirement is 500K miles)
- Response time: 1 sec or less (time response must be 5 ms for cylinder-to cylinder monitoring, can be 50-100 ms for engine control)

- Separately measure NO and NO₂ (to evaluate treatments)
- Must be immune to soot, sulfur, and urea (NH₃)

Recommendations/Issues:

- NO and NO₂ need to be measured independently. Ceramic NO_X sensors based upon zirconia electrolyte are now available. Issues are sensor durability and cost (many electrical leads are required). Existing sensors are slow. Ammonia interference is a problem (this may not be a problem depending on where the sensor is located). Another big issue is the electronics the sensors are required to measure sub microamps to measure low ppm concentrations. Sensor drift is a problem.
- Fundamental science is important for the ceramic-based sensor. National labs can contribute with their surface catalysis expertise. These sensors are essentially small catalytic converters, and the surface chemistry is not understood. Universities can also contribute. Prof. Göpel's group at the University of Tubingen in Germany has done some surface modeling. Perhaps some of the combustion modeling work performed by DOE labs can be extended to the NO_X sensor. The work should be precompetitive to avoid proprietary or confidentiality issues.
- There are other potential technologies to consider, such as spectroscopic. There has also been work performed at ANL on a microwave NO_x sensor, although high cost may be an issue. There is high risk (cost and time) involved with pursuing a route other than the ceramic type NO_x sensors.

Particulate Sensors

Requirements:

- Maximum smoke number will be below 2 BSU (Bosch smoke units)
- Minimum detection: 0.2 BSU
- Response time, lifetime, and temperature requirements are the same as for the NO_x sensor

Recommendations/Issues:

 Measure total particulate mass. Industry works on Bosch number or opacity for smoke measurements rather than particle number and size distribution. Industry is more interested in particulate mass (e.g., grams per mile or grams per second) rather than particle characteristics. Integrate over all particle sizes. Different engines have different particle size distributions. Particle size determines whether the particle is retained in the human lung and the extent of health effects. The Micro-Orifice Uniform Deposit Impactor (MOUDI) unit measures particle sizes from 0.05 to 10 microns (cascade impactor device). Linkage between Bosch number and actual particle mass loading is unclear. Particle size distribution will impact the optical attenuation (Bosch unit). PM sensor will be located either in each cylinder exhaust or at the tailpipe. A PM sensor could possibly be combined with a HC sensor.

- Industry needs to develop minimum performance requirements for the particulate sensor. The measurement can be performed optically although the sensor window will need to be baffled to avoid soot deposition on the window. Bosch smoke unit numbers need to be correlated with particle mass loading.
- There are no commercial PM sensors available for on-board measurements. The only PM sensor under development is at Argonne National Laboratory. Sensor specifications are likely to be highly engine-dependent because different engine manufacturers will have different performance specs. Improved dialogue needs to be established between auto manufacturers, sensor developers, and OEMs for development of a viable PM sensor to develop specifications such as mass loading range, time response, accuracy, and temperature range.
- Pursue two paths for development: improve the "ring-electrode" type or modify existing optical smoke measurement instrumentation (scatterometer, Bosch smoke meter, etc.) for low-cost mass production.
- Barriers to a viable PM sensor :
 - Temperature
 - Exhaust environment
 - Cost requirements
 - Lifetime, durability
 - Packaging for onboard measurement
 - Interact with auto computer to ensure sensor is "vehicle friendly"
 - Optical access..."crudding up the optical window"
 - Particle size...future smaller engines will be more difficult
- Universities and national labs could contribute to the solution to this problem, providing the base technology. A collaboration among universities national lab researchers, OEMs, and the customer (auto manufacturers) should be established.
- CARB may have role in setting sensor requirements because they must approve the measurement system based on regulatory requirements.
- The near-term introduction of diesel autos makes development of the PM sensor time critical. There may be different timetables for light-duty and heavy-duty vehicles. The market for this sensor is potentially every diesel vehicle in the world.

Wide-Range Oxygen Sensors

Requirements:

- Range is lambda from 0.7 to 15 (includes diesel)...wide range gives you better control but costs more
- Response better than 4 Hz for engine control
- Current sensors are expensive (multi-layer ceramics) need to get cost down to \$20
- Temperature range from ambient to 1000 °C (same as for NO_x sensor)
- Need fast startup time (<15 seconds)
- Resistant to poisoning from phosphorous, sulfur, lead and particulates (soot)

Recommendations/Issues:

- Wide-range oxygen sensors are too expensive because of small production quantities.
 Current manufacturers are Delphi, NGK Sparkplug, Bosch, and Denso (Toyota).
 Better sensor start-up algorithms are needed. LANL had a patent issued in 1996 for a lean-burn system which measures transfer of oxygen through thick films of transition metal oxides resistant to particulate plugging and poisoning. This sensor may only be applicable to lean burn measurements, not rich mixtures. The lean-only use may be particularly applicable to diesel engines.
- EPA should mandate tighter control on stoichiometry; otherwise lean burn O₂ sensors will continue to dominate.
- Durability for heavy-duty applications is an issue. Diesel engine manufacturers have an interest in this sensor (e.g., for identifying a bad injector or for "trimming out" injectors). Sensor can be poisoned by sulfur. Because of the high cost, the automotive systems folks have found a way to do without this sensor.
- Large resources are required to develop new sensor.

Table 4. Summary of Sensor Needs for CIDI/SIDI Engines

		State of Development/
Sensor	Rank	R&D Need
NO_x	High	Electrochemical ceramic oxide sensors exist, but do not meet needs. Several
		efforts to improve this type of sensor underway at national labs and at sensor
		manufacturers. Fundamental scientific understanding needed on surface
		chemistry. Alternative technologies might also be looked at, but high risk (cost
		and time) involved in pursuing other than ceramic NO _x sensors. However, long
		term, high-risk projects are appropriate for national labs and universities.

PM and smoke	High	For CIDI only. Some variation in need expressed by different auto
		manufacturers. Need to look at in many dimensions including size and chemical
		properties. Minimum performance requirements need to be set. No commercial
		sensors exist for on-board measurement. It may be possible to further develop
		existing technology, but not likely. Collaborations involving national labs,
		universities, OEMs, and auto manufacturers needed.
Wide-range	Medium	Wide-range oxygen sensors exist but do not meet the cost constraints. Want a
oxygen		broadband response and not a switch, i.e. a proportional sensor. Need better
		sensor start-up algorithms, but need requirements specified by the systems
		people. Control strategies have to be developed for non-stoichiometry which
		utilize the fact that if you go lean you need a proportional sensor. Need dialogue
		between system and hardware people. Efforts should be directed at
		manufacturing cost reduction and robustness. Partnerships between national
		labs, sensor manufacturers, and auto manufacturers are needed.
Ammonia	Medium	For CIDI only and only if use urea SCR. Cannot have ammonia slip after
		catalyst. No sensor currently exists which meets the needs. No consensus to put
		a lot of resources into development of this sensor.
Hydrocarbons	Medium	No sensor available commercially which meets needs. Several efforts underway
		at national labs. No pressing need to initiate new efforts as long as current
		development work continues. However, need exists for more basic research and
		engineering of devices.
EGR	Medium	Current sensors exist for measuring EGR flow. Any additional needs are very
		system/strategy dependent.
Time-resolved	Medium	Includes measurement of combustion parameters, misfire, and in-cylinder
exhaust		pressure. Some sensors exist. Additional needs are very system dependent.
temperature		
Mass air flow	Medium	Sensors exist. Additional needs are very system dependent.
High	Medium	Good sensors really do not exist but requirements are system dependent. Need
performance		instantaneous torque.
torque		
Fuel composition	Low	Little interest in sensors for fuel composition or volatility.
Carbon	Low	Only needed for fuel cells, not much for CIDI/SIDI.
monoxide		
Sulfur content in	Low	No need seen for sensors. R&D need is how to get sulfur out.
fuel		

It was noted that there are suppliers developing in-cylinder pressure sensors and torque sensors and that both of these are very system/strategy dependent. However, the group expressed no interest in developing an in-cylinder pressure sensor. In addition, a better resolution crankshaft position sensor was discussed, with limited interest.

While many of the sensors identified above currently exist for defined applications, it is the consensus that there are no sensors available that fall into the highest need category and meet the combination of specifications required by the automotive industry. These specifications include operation in very harsh environments, high sensitivity and selectivity, long lifetime, low/no maintenance, high stability, and low cost, among others. For PM sensors noted deficiencies are: durability, operation at high temperature, cost, and the tendency of window to foul. NO_x sensors currently exist, but they are too complex and costly. Basic understanding of surface chemistry is needed. One particular theme which appeared to run through much of the discussion in the CIDI/SIDI session was that sensors need to be developed for specific systems, not generic operation, due to differences in manufacturers' measurement strategies.

Appendices

- A. List of Participants
- B. Agenda
- C. Visual Aids from Technical Presentations

Plenary Session

- Overview of the DOE Transportation Fuel Cell Program-JoAnn Milliken
- Sensor Performance Requirements for Compression-Ignition, Direct-Injection Engines-Ken Howden
- Spark Ignition Direct Injection Engine R&D-Rogelio Sullivan
- Driving Towards Clean Air: Countdown to Zero-Tom Cackette
- State of Development of PEM Fuel Cells-Doug Wheeler
- State of Development-CIDI Engines-Rich Belaire
- Sensors: An Overview-Joseph Stetter

Fuel Cells Session

- A Critical Look at the Maturing Development and Utilization of Optical Sensor Technologies-Jacob Wong
- Gas Sensors for Fuel Cell Process Monitoring-Shuh-Haw Sheen
- Sensor Functions in Fuel Cells-Doug Wheeler

CIDI/SIDI Session

- Review: National Laboratory Sensor Projects for CIDI/SIDI Engines-Richard Cernosek
- Sensor Priorities from a Supplier Standpoint-Joe Giachino
- University-Based Sensor Research-Brage Golding

- Real-Time Sensors for Intelligent Control of Automotive Engines and Processes-A. C. Paul Raptis
- Diesel Closed-Loop Control Via Smoke Sensor-Frank Zhao
- Ford Motor Company Sensor Program-Rick Soltis